

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁴ : C08G 81/02, H01M 6/18 C08G 65/08</p>	<p>A1</p>	<p>(11) International Publication Number: WO 88/ 03154 (43) International Publication Date: 5 May 1988 (05.05.88)</p>
<p>(21) International Application Number: PCT/GB87/00759 (22) International Filing Date: 27 October 1987 (27.10.87) (31) Priority Application Number: 8625659 (32) Priority Date: 27 October 1986 (27.10.86) (33) Priority Country: GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Whitehall, London SW1A 2HB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : GILES, Jeremy, Roger, Martin [GB/GB]; Royal Aircraft Establishment, Farnborough, Hampshire GU14 6TD (GB). MACCALLUM, James, Richard [GB/GB]; 9 Cairnsden Gardens, St Andrews (GB). GRAY, Fiona, Mary [GB/GB]; Chemistry Department, University of St Andrews,</p>		<p>The Purdie Building, St Andrews KY16 9ST (GB). VINCENT, Colin, Angus [GB/GB]; 1 Station Brae, Newport on Tay, Fife (GB). (74) Agent: BECKHAM, Robert, William; Procurement Executive, Ministry of Defence, Patents 1A(4), Room 2014, Empress State Building, Lillie Road, London SW6 1TR (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: POLYMERIC ION CONDUCTORS</p> <p>(57) Abstract</p> <p>ABA triblock polymers, the A block being rigid having a transition away from its rigid phase above 70°C, the B block being wholly or partly ion-coordinating, elastomeric or amorphous, the B/A block length ratio being greater than 1. When the B block is complexed with an ionic salt these polymers act as polymeric electrolytes which may be used in cells etc. Preferred polymers are those where HC=CH sites in the polybutadiene segment of a polystyrene-polybutadiene-polystyrene polymer are replaced by -CH₂CH-X-(CH₂CH₂O)_m-R, where X is a link, R is alkyl. A preferred salt is LiCF₃SO₃.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

POLYMERIC ION CONDUCTORS

This invention relates to polymeric materials; in addition this invention relates to ionically conducting polymeric materials and their preparation and their use in cells, for example galvanic cells, or other electrical or electrochemical devices, or heterogeneous phase processes, for example, solute separation and extraction.

The electrolytes most commonly used in electrolytic cells are liquids in the form of solutions containing ionic species, which allow migration of ions between the electrodes of the cell. The electrolytes used suffer from several disadvantages in that they are often corrosive and toxic and present handling and storage difficulties through spillage or leakage from the cell.

In order to overcome the disadvantages inherent in liquid electrolytes and to obtain superior long-term storage stability there is interest in solid polymeric electrolytes in which ion mobility is achieved through coordination by sites on the polymer chain of electrolyte ions thus promoting electrolyte dissolution and salt dissociation. One polymer which has been examined extensively for this application is poly (ethylene oxide). It is able to form stable complexes with a number of salts, however the electrical and mechanical properties of such electrolytes require further improvements before application is appropriate, especially for cells required to operate at or near ambient temperature. A major problem with poly (ethylene oxide) electrolytes at temperatures below 60°C is their high crystallinity and the associated low ion mobility.

Recent advances in the field of polymeric electrolytes have been based on the modification of the polymeric structure in order to increase ion mobility and maintain a high value of such over a wider temperature range.

Routes to achieve this have been disclosed in UK Patent Applications 8421193 and 8421194 and in UK Patent Application 8520902, claiming priority from the earlier applications. The routes involve the use of for example, an oxyalkane coordinating unit in the form of an oligomeric sequence such as poly (ethylene glycol) linked by flexible groups at -OH termini to form both linear or crosslinked

polymers, so that crystalline, non-conducting phases are essentially eliminated. The physical form of the electrolyte prepared can be controlled by the nature of the constituent parts of the resultant electrolyte and the degree and nature of any crosslinking.

5 This invention is concerned with the use of an alternative class of polymer for use as electrolytes whereby the largely amorphous nature of the material, necessary for high ion conduction is retained yet the mechanical integrity is sufficient to allow application in a useful device. Alternative routes to enhanced mechanical integrity, described
10 in the patent application 8520902 include the use of filler particles or the introduction of controlled crosslinking.

According to a first aspect of the invention there is provided a novel polymer, comprising an ABA triblock copolymer; the A block material being rigid having a transition temperature away from its
15 rigid phase above 70°C, the B block material being wholly or partly ion-coordinating, elastomeric or amorphous, the B/A block length ratio being greater than 1, and in which phase separation between the A and B blocks may or may not occur.

If phase separation does occur it is preferred
20 that the A block forms phases or domains embedded in a matrix of the B block.

In forming a rigid phase the A block polymeric component is either glassy and below its glass transition temperature or predominantly crystalline and below its melting point, when in the intended temperature
25 range of use.

The B block polymeric component has a glass transition temperature below the intended operating temperature range, and ideally as low as possible, eg -20°C or preferably even lower, eg less than -40°C.

The intended temperature range of use, or operating temperature
30 range is generally around ambient, eg 20°C or above, eg up to 60°C.

It is preferred that phase separation between the A and B blocks occurs, as mentioned above, and this may be encouraged or caused to occur by making a blend of the polymer with a polymer which is compatible with the A block material and incompatible with the B phase
35 component. By 'compatible' herein is included miscible without phase separation.

Phase separation and aggregation of A blocks occurs as a result

of the thermo-dynamic incompatibility of the component blocks. The rigid domains of A block form throughout the polymer and may form a relatively rigid macrolattice.

A polymer of this type, having a B block which is elastomeric, of low glass transition temperature (below the required operating temperature range) and ion coordinating resulting in a high ion mobility, and A blocks which form rigid phases or domains which soften or melt at high temperatures eg above 70°C, and are embedded and dispersed within the surrounding elastomeric or amorphous phase may have physical properties which can easily be controlled, for example, the tensile strength. This aspect is a most important part of the invention: the ability to control the mechanical properties eg to obtain a high modulus and low creep characteristic while maintaining a conductivity, obtained from high frequency ac impedance methods of greater than 10^{-6} and preferably greater than $5 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C and simultaneously having a thermoplastic material, which may be soluble in an appropriate solvent.

Having a B phase of low glass transition temperature, polymers of the invention may be used as components of polymeric electrolytes. For these electrolyte forming polymers of the invention it is preferred that the A blocks are of equal length. The B/A block length ratio is controlled, with length (B) greater than length (A), so that the preferred morphology, of near spherical domains of A surrounded by elastomeric B regions, is adopted.

The lengths of the A blocks and the B/A block length ratio will also influence the occurrence or non occurrence of phase separation in the polymer.

Suitable A block lengths and B/A ratios to achieve phase separation will be apparent to those skilled in the art, and are for example described in 'Encyclopaedia of Polymer Science and Technology' 15 (1971) (pub John Wiley and Sons) and also in H G Elias 'Macromolecules' 2nd Edn 1 (Plenum Press).

The size of the A block phases or domains when phase separation occurs may also be dependent upon the block lengths, and larger block lengths will lead to larger phases or domains. The exact morphology of the A domains will also depend upon physical treatment

received by the polymer, for example solution casting, melt forming and any applied stress. For example stretching or extrusion is likely to elongate or flatten the domains. Blending of the ABA triblock copolymer of the invention with an A-phase compatible material, as
5 mentioned above, may also be used to influence the size and/or shape of the A block domains. If the added material has a high glass transition temperature and the subsequent blended A phase retains a glass transition temperature above 70°C, then the blending polymer may be used to increase the volume fraction of the rigid A phase, and
10 hence alter the physical properties of the polymer.

It is preferred that the average A block diameter for the preferred spherical domains is less than 1 μm , preferably less than 1000 Å.

Such domain sizes are generally sufficient to produce a
15 high modulus material without impairing the conducting nature of the B phase.

Materials according to the invention may also be made with anisotropic physical (eg the extent of swelling caused by a solvent selective to the B block), mechanical or ion conducting properties.
20 This anisotropy may be achieved by modification of the A/B block size ratio, the forming and manipulation of the material (eg solvent casting, melt forming, extrusion), and/or blending of an ABA triblock copolymer with an A-block compatible polymer as described above.

These parameters and methods, individually or in some combination
25 may be used to generate rigid A phase regions (domains) of various shapes, sizes and relative location, isolated or interconnected in some manner. For example the A domains may adopt shapes which are essentially spheres, lamellae or cylinders (fibres), the non-spherical shapes giving rise to anisotropy.

30 The general morphological properties of ABA triblock copolymers are described by H G Elias (given above) and by D C Allport and W H Janes in 'Block Copolymers' 1974 (Applied Science).

Blends of the ABA triblock polymers of the invention with materials other than or in addition to A-compatible materials may be made. For example, a polymer, oligomer, or low mass substance or combination of such may be blended with the ABA copolymer, being compatible with

the B block component and incompatible with the A phase component. This possibility may be used to provide physical and material contact with the surroundings of the ABA triblock copolymer when in its application environment. Such an agent added to and blended with the B phase component may act as plasticizer by lowering the glass transition temperature of the phase. In the formation of an electrolyte material the added agent may also be ion coordinating; for other applications the added agent may perform another active function.

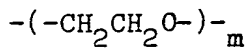
Alternatively materials may be blended with the ABA triblock copolymer which are compatible with both the A and B blocks of the copolymer. Additionally or alternatively blends using the ABA triblock polymers of this invention may be formed by introduction of substances to both the A and B block phases so that three or more starting substances are used in the preparation of the required material.

The quantity of material which is blended with the ABA triblock copolymer may be limited by the necessity to retain desirable physical and/or conduction properties, whether the added material is blended with the A or B block.

It has been found that in many cases the blended mixture may contain a 2:1 weight ratio of ABA triblock copolymer and blending agents without detriment to at least the conducting properties of the material, and in the case of a B-compatible blend an improvement in the conductivity relative to the ABA triblock copolymer alone is possible.

The chemical nature of the B and A blocks will now be discussed.

The B blocks are ion-coordinating, and the atom in the B block responsible for ion coordination is preferably oxygen in an oxyalkane sequence, preferably a polyoxyethylene sequence, ie:



where m is an integer, or in an epoxide $\text{CH}-\text{CH}$ or hydroxy $\text{CH}-\text{OH}$ group. This sequence may be present in either the B block polymer main chain or in side chains or cross links attached to the B block chain. The ion coordinating B block is elastomeric or amorphous. It is therefore desirable to have only short oxyalkane sequences or oligomers either as main chain, side chain or cross link components so as to reduce

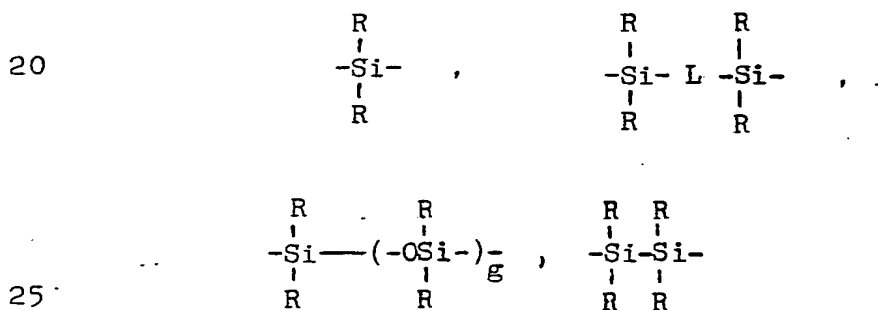
the amount of ambient temperature crystallisation. Alternatively, when m is rather high, B-block plasticisers may be mixed with or blended with the polymer, for example low mass (less than ca 800) polyethylene glycol dimethyl ether.

When the oxyalkane sequence or oligomer is present in the main chain of the B block, m should be an integer 3 - 10, and when in a side chain or cross link, 2 - 22 for example 7 - 17.

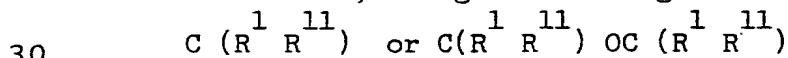
These oxyalkane sequences or oligomers may be linked together or linked to the B-block chain (when present in a side chain) by chain extender or linking groups or sequences thereof. These are desirably flexible to increase polymer chain mobility.

The links between the oxyalkane sequences or oligomers or between these and the B block main chain may be or include ether links (-O-), methylene (-CH₂-) ester (-COO-), urethane (-NH-COO-), phosphazine, phosphate ester, siloxane or combinations of these such as {CH₂}_n where n is 2-12 ('polymethylene'), -(CH₂)_n-NHCOO- and oxymethylene -OCH₂-.

Other suitable linking groups include those described in UK Patent Applications 8421193, 8421194 and 8520902, for example

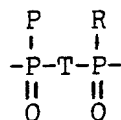


where each R is independently selected from C₁₋₂₀ alkyl; L is -O-, 1,4 - phenyl, -(CH₂)_n or -(CH₂CH₂O)_m, m being as defined above, and n is less than 12, and g is an integer between 1 and 100.



where R¹ and R¹¹ are independently selected from H, C₁₋₂₀ alkyl alkanoyl, or alkoxy.

and



5

where R is alkoxy, preferably methoxy or ethoxy, and T is -O-,
-O(CH₂CH₂O)_t- where t is 1 to 12.

The B block may also contain covalently attached anions, such
as -CF₂CF₂SO₃^θ

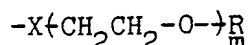
10

It is preferred that the B block polymer is essentially free from crosslinking or that the crosslink density is low such that the B block behaves as a linear chain elastomer. In order to generate an oxyalkane copolymer of a sufficiently high molecular weight so as to act as an effective B block, a low concentration of crosslinks may be necessary.

15

The polyoxyalkane sequences or oligomers are preferably attached to the B block main chain by a linking group, and may be terminated by hydrogen or by an alkyl group containing 1- 6 carbon atoms so that the side chain has a structure:

20

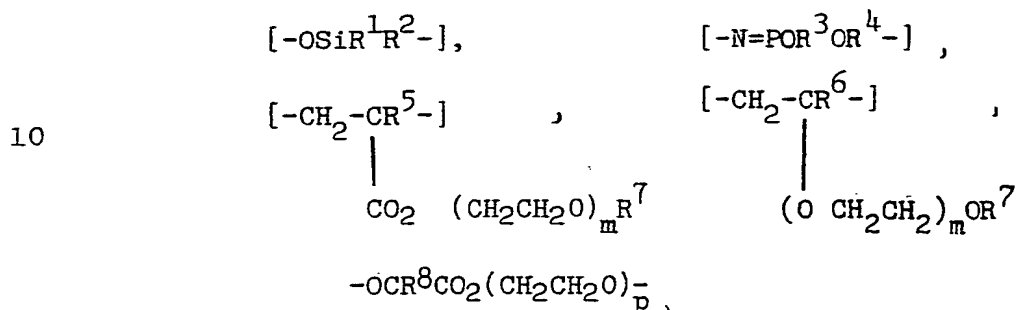


where m is as defined above, X is the linking group and R is the alkyl or hydrogen, methyl being preferred. m is preferably chosen so as to give the polyoxyalkane side chain (not counting X) a molecular mass between 100 and 850, for example 750.

25

The B block polymer main chain may have a variety of structures. A preferred structure is one derived from a cis-1,4 polybutadiene chain onto which are grafted the preferred polyoxyalkane sequences or oligomers, at some of the unsaturated sites in the chain, using a suitable linking group X as described above to link the polyoxyalkane
30 sequence to the main chain.

Other suitable polymers for the B block include those described in UK Patent Applications 8421193, 8421194 and 9520902 where main-chain, side-chain and crosslink oxyalkane, preferably oxyethylene, sequences or oligomers derived from, for example, siloxane, methylene or phosphate ester groups or groupings are described. Additional preferred structural types include main chain homo or co polymers containing the units:



where R^1 and R^2 are independently selected from C_{1-6} alkyl, preferably methyl or ethyl, or $-(\text{CH}_2)_d(\text{OCH}_2\text{CH}_2)_n\text{OR}^7$ or $-(\text{OCH}_2\text{CH}_2)_n\text{OR}^7$ where n is 2 - 22 and d is 2 or 3, R^3 and R^4 are independently selected from C_{1-6} alkyl, preferably methyl or ethyl or $-(\text{OCH}_2\text{CH}_2)_m\text{OR}^7$ where m is 2-22, $\text{R}^5 - \text{R}^7$ are independently selected from $\text{C}_1 - 6$ alkyl and H, and are preferably H or CH_3 , R^8 is $-(\text{CH}_2)_g$ where g is an integer 2 - 8 and p is an integer 3 - 10, defining the average length of the oxyalkane units.

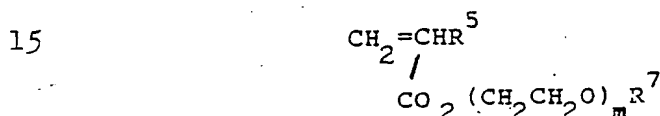
The preferred materials for the A blocks are described below.

It is desired that the A phase is rigid and softens or melts above 70°C . It is also preferred that there is no appreciable crosslinking in the A block component so that the triblock copolymer may be soluble in a known solvent. Thus any polymer of high glass transition, and, or alternatively, with a high melting transition and a large crystalline content, that is incompatible with the chosen B block component, may be used. Suitable polymers for the A block component include polystyrene, poly (α - methylstyrene) polyurethanes and poly (p-xylylene), and these are preferred.

In preparing a required ABA triblock copolymer a number of synthetic approaches are possible. Either the preferred B block polymer may be formed and the A blocks polymerised onto the B block chain ends, or alternatively the A blocks may be independently polymerised and then bonded to the chain ends of the preformed B block. Other methods of preparation will be apparent to those skilled in the art.

Examples of suitable methods for preparing the ABA polymer chain are discussed below.

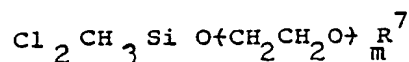
Where a copolymer is formed, which is to act as the B block, then for example, any suitably substituted vinyl monomer may be copolymerised, where possible with a vinyl monomer derived from the preferred structural types given, where this is possible, for example:-



Techniques for this include the 'Iniferter' method described by T Otsu and A Kurigama, Polymer Journal 1985, 17, 97.

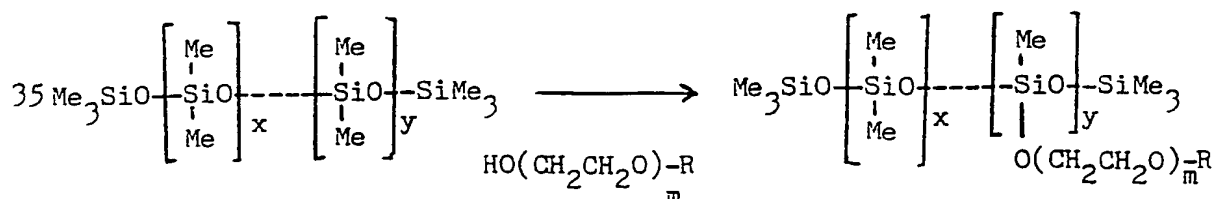
Routes to the synthesis of oxyalkane side-chain containing polysiloxanes are described in British Patent 892, 819 and similar methods may be used in this invention or may include methods described by W Noll in 'Chemistry and Technology of Silicones' Academic Press, 1968.

For example these polysiloxanes may be prepared by the controlled hydrolysis of compounds of the type:



which may be prepared by the reaction of mono-alkoxy, eg methoxy terminated polyethylene glycol (PEG) with CH_3SiCl_3 . Under appropriate conditions the dichloro product is formed, HCl being eliminated.

These polysiloxanes may also be prepared from commercially available poly (hydrogen methyl/dimethyl siloxanes) by a reaction such as:



Me = methyl, x and y are large integers.

The phosphazine based polymers ($-N=POR^3OR^4-$) may be prepared, first by forming poly (dichlorophosphazine) ($-N=PCl_2-$) and then allowing this to react with the required glycol or sodium salt thereof, here $R^3 = R^4$.

In another method, a poly (ethylene glycol) of suitable molecular weight, eg 400 is reacted with dichloro or dibromo methane in basic conditions, eg in the presence of KOH as described in GB 8520902 to form an elastomeric polymer of high ionic conductivity when complexed with for example $LiCF_3SO_3$.

If the synthetic conditions are chosen such that the end groups of the polymer are $-CH_2 Br$ (eg an excess of dibromomethane) then a photochemically initiated radical polymerisation of the A block monomer, for example styrene, can be initiated to yield the desired triblock copolymer. Alternatively, if the B block polymer just described has $-CH_2OH$ end groups then these may be reacted with an alkyl diisocyanate to yield a polymer with isocyanate end group functions; the polymer so formed may be further reacted with cumene hydroperoxide to form peroxy end group functions which can be cleaved to form free radical active centres and thus again initiate A block formation in the presence of a suitable monomer, for example styrene.

A further ABA triblock copolymer with A blocks composed of linear polyurethane segments formed from a diisocyanate and low molecular weight glycol, preferably poorly or non salt coordinating, and B block from the above described polymer generated by reaction of poly (ethylene glycol) Mwt 400 with dibromo or dichloro methane and having CH_2OH end groups may be prepared as follows. The B block polymer may be treated with a diisocyanate, aliphatic or aromatic to generate a polymer, isocyanate end-group functionalised. This polymer may now be reacted with further diisocyanate and a low molecular weight glycol to form the A blocks. Alternatively a preformed polyurethane may be bonded to the B block polymer, with the end groups of each A or B block forming polymer chosen in order to allow urethane linking. A catalyst may be used, and in general techniques and reagents described in the 'Encyclopaedia of Polymer Science and Technology' Volumes 11 and 15 may be employed.

A further synthetic procedure, preferred and generally applicable,

is to modify the B block sequence of an existing or preprepared ABA triblock copolymer by grafting on oxyalkane sequences as side chains at appropriate positions.

This requires suitable functional groups or unsaturated sites on the B block chain which may be reacted with functional termini on the oxyalkane sequence either directly or indirectly. The possible chemistry is limited by the need to restrict as far as possible any cross linking between the B blocks.

10

A preferred starting point is an ABA triblock copolymer having a B-block which is poly (cis-1,4 butadiene). Here there is the possibility of an addition reaction leading to grafting at one or both carbon atoms of each carbon - carbon double bond. The A block component may be one of the preferred polymers referred to above, so that this starting point is for example a polystyrene - poly cis -1,4-butadiene-polystyrene ("PS-PBD-PS") ABA triblock polymer. These starting materials are either commercially available or may be prepared by known methods.

A method grafting oxyalkane sequences onto such a B block involves epoxidation of C=C groups, followed by reduction to generate -OH functions for use in the bonding of the oxyalkanes, appropriately terminally functionalised. Suitable reagents for the first two steps are m-chloroperbenzoic acid and LiAlH_4 respectively. Their use leads to a minimum number of unwanted side reactions. By controlling the epoxidation step, eg via stoichiometry, introduction of the required degree of -OH functionalisation may be achieved.

The method of epoxidation of the diene is preferred as this reduces the possibility of cross-linking.

Having introduced these -OH groups into the B group, grafting in the polyoxyalkane sequence is facilitated. Preferred methods are to form an ether link via for example formation of a tosyl - terminated polyoxyalkane sequence and reaction of this with the -OH groups, or formation of urethane links, by formation of an isocyanate-terminated polyoxyalkane sequence and reaction of this with the -OH groups.

Other types of link are also suitable in these polymers, for example ester links formed by reaction of a carboxylic acid terminated polyoxyalkane sequence with the -OH group of the B block of the polymer.

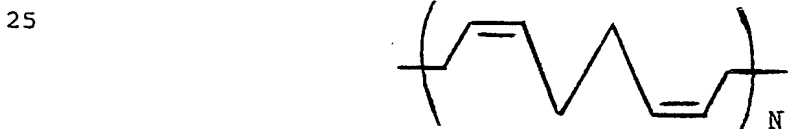
A particularly preferred ABA triblock polymer of the invention which may advantageously be prepared from an existing PS-PBD-PS polymer using the above method therefore has a B block in which random replacement of a proportion of unsaturated HC=CH sites in the PBD chain are replaced by



sites, where X, m and R are as defined above. For inter alia convenience of preparation, the linking group X may be an ether-type linkage (ie X is an oxygen atom), or a urethane-type linkage (eg X is -OCO.NH(CH₂)_nNHCOO where n is 2-12), or a dicarboxylate linkage (eg X is -OCO-(CH₂)_p-COO- where p is 1-12, preferably 2). R is preferably methyl.

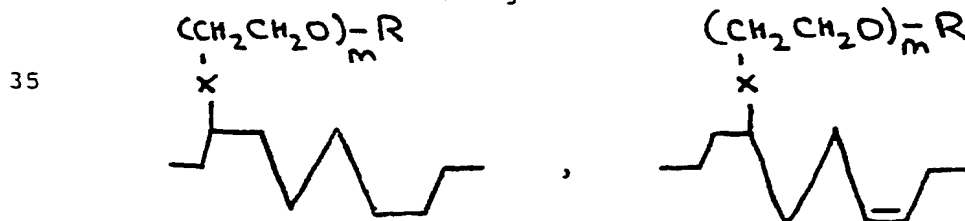
The proportion of C=C sites in the PBD chain which are replaced in this way will be related to the degree of -OH functionalisation that is introduced if the epoxidation - reduction process above is followed. Typically but not exclusively a preferred proportion of replacement is 20-60%.

The structure of poly cis -1,4 butadiene is shown ideally below:

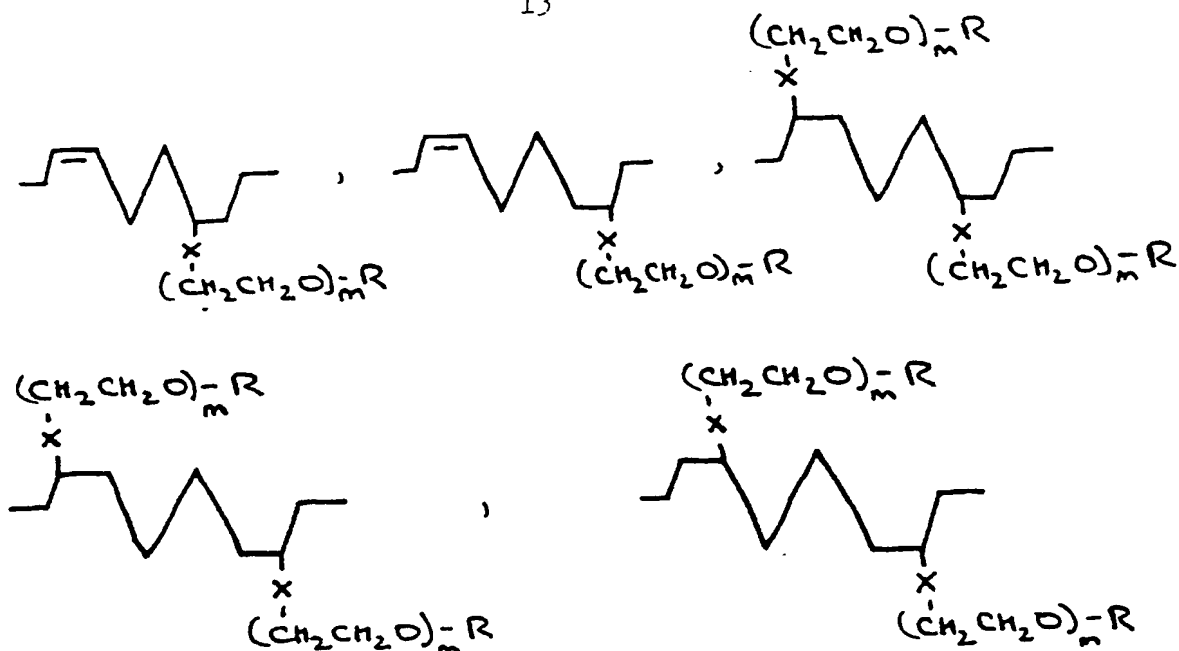


where N is a large number. The polymeric chain has at least 80-85% of the double bonds in the cis - configuration.

The B block of the particularly preferred polymers of the invention will therefore contain such repeating units, and may also contain a proportion at least of randomly distributed units having structures selected from the following:



13



where single and double bonds are shown conventionally by line formulae
 10 and X, M and R are as defined above.

For a polymer as described above having polyoxyalkane side chains
 grafted onto the PBD B block the preferred average molar masses in the
 starting material for the A-block polystyrene segments are about 10,000-
 40,000 each and for the B block about 40,000 up to about 150,000
 15 typically about 100,000. These molar masses are found to give the
 desired structure of the polymer as discussed above.

For blending with the polymer mentioned above, a suitable A-
 compatible blending material is polystyrene, when the A block is also
 polystyrene, and may have a similar molar mass to that of the A block
 20 eg 20,000. A suitable B-compatible blending material is for example
 polyethylene glycol dimethyl ether (of average molar mass ca 400),
 polyethylene glycol or other low molecular mass (eg ca 400) material
 when for example the B block is methoxy polyethylene glycol grafted
 polybutadiene.

25 The polymer may also be blended with high molar mass polyethylene
 oxide, for example of molar mass $1-6 \times 10^6$.

When it is desired to blend both A block and B block compatible
 material with this preferred polymer then the A- and B- block
 compatible materials referred to above may be used.

When the starting point for the epoxidisation and -OH functionalisation process described above is an ABA triblock polymer having a PBD B-block and A blocks which are the preferred A-block polymers mentioned above, in particular polystyrene, the epoxidised or -CH functionalised intermediates may also be novel and useful materials.

Accordingly the invention further provides a polymer having a structure based upon an ABA triblock copolymer in which the A-blocks are selected from polystyrene, poly (α -methylstyrene), polyurethanes and poly (p-xylylene), especially polystyrene, and the B-block is a poly-cis 1,4-butadiene chain in which a proportion at least of the HC=CH sites in the B-block are replaced by HC-CH or HC-CH₂ sites.

These epoxidised and hydroxy-functionalised polymers may be ion coordinating by virtue of the presence of the oxygen atom in the epoxide or hydroxy group in the PBD B-block, and therefore they are encompassed by the polymers of the first aspect of the invention described above. They may therefore be made into polymeric electrolytes by inclusion of an ionic salt.

As well as being intermediates for the preparation of other polymers by grafting side chains onto the -OH functional groups, or as a base for polymeric electrolytes, these epoxidised and -OH functionalised polymers may also be used for other purposes, eg structural polymers. The epoxidised material at least has properties similar to the epoxidised natural rubber referred to above.

A further preferred ABA triblock polymer of this invention is one in which the A blocks are selected from polystyrene, poly (α -methylstyrene), polyurethanes and poly (p-xylylene), preferably polystyrene, and the B block consists either wholly of polyethylene oxide, ie $(CH_2CH_2O)_m$ sequences, or of $(CH_2CH_2O)_m$ sequences joined by linker groups. This polymer has the polyethylene oxide sequences in its B block main chain.

In a preferred embodiment of this type of polymer, the B block consists ideally of two (CH_2CH_2O) sequences joined at or close to the mid point of the B block by a linker group. Preferred linker groups in this case include the links between the oxyalkane sequences or oligomers discussed above, ie they may be or include ether, methylene, ester, urethane, $(CH_2)_n-NHCOO-$ and oxymethylene OCH_2 .

Such an ABA triblock polymer may be prepared by first preparing an A-polyethylene oxide diblock polymer with a functional terminus, particularly $-OH$ on the polyethylene oxide segment. Two such diblock polymers may then be combined via a suitable linking molecule to form a linking group in the resulting ABA triblock copolymer. For example two such diblock polymers may be reacted with a dihalomethane and potassium hydroxide to leave a $-CH_2-$ linker when the functional terminus is $-OH$. Alternatively a diisocyanate such as $OCN-(CH_2)_r-NCO$ where r is an integer may be used when the functional terminus is $-OH$ to form a urethane link eg $-OOCNH(CH_2)_r-NHCOO$. Alternatively a dicarboxylic acid, or an anhydride such as succinic anhydride may be used to introduce an ester linker, eg $-OOC(CH_2)_r-COO$ when the functional terminus is $-OH$. Other linkers which are suitable for joining two $-OH$ terminated polyethylene oxide sequences will be apparent to those skilled in the field.

As above typical molar masses for the A blocks are 10,000 - 40,000 and for the B block about 120 - 3,000 preferably as low as possible. Short polyethylene oxide sequences are preferred.

The ABA triblock copolymers of the invention may be used to form a polymeric electrolyte, and according to a further aspect of the invention there is provided a polymeric electrolyte comprising an ABA triblock copolymer as described above and having an ionic salt
5 complexed with the B-block. This electrolyte is therefore a solid solution electrolyte.

For use in electrolytes, polymers in which phase separation of the A blocks, as described above, has occurred, are preferred, for example those based upon a PS-PBD-PS ABA triblock polymer as described
10 above.

The ionic salt complexed with the B block of the ABA triblock copolymer to form a solid solution electrolyte is preferably the salt of an alkali or alkaline earth metal, this includes lithium, sodium, magnesium, potassium or calcium salts; alternatively an ammonium or
15 alkyl ammonium salt containing the cation R_4N^+ where the R groups are selected from alkyl, optionally substituted alkyl or H, may be used. The anion of the salt may be any commonly used anion, but is preferably a relatively large anion of a strong acid, for example, perchlorate ClO_4^- , trifluoromethanesulphonate $CF_3SO_3^-$, BF_4^- , PF_6^- , SCN^- ,
20 $CF_3CO_2^-$, $CH_3CO_2^-$, I^- or $B(C_6H_5)_4^-$ or I_3^- . $LiCF_3SO_3$ is a preferred salt.

Alternatively if the B block contains covalently attached anions, eg $-CF_2CF_2SO_3^-$ with associated ionically-bound cations eg Li^+ ions, an added salt may be unnecessary, or a salt may be added.

The polymeric electrolyte of this aspect of the invention may
25 be made in a number of ways, all intended to disperse and dissolve the salt in the ABA triblock copolymer.

Known methods may be used, for example mixing together the polymer and salt and then melting them together to form a complex and then
30 extruding the mixture into a thin film.

Another method involves milling the salt and the polymer together at a low temperature, followed by forming the electrolyte into a film with heat and pressure.

A third method involves dissolving the salt and the polymer
35 together in a suitable solvent at an appropriate concentration, and forming the mixture into a film by solvent evaporation. Suitable solvents include for example THF. Some solvents such as

nitromethane encourage phase separation between the A and B blocks, and the use of such solvents is preferred as this has in some cases been found to lead to improved electrolyte performance. Mixtures of solvents may also be used.

5 In a further method, the polymer may be immersed in a solution of the salt in a suitable solvent which does not dissolve the polymer, eg an alcohol such as methanol. The salt thereby partitions between the solution and the B block of the polymer, and is incorporated into the polymer.

10 In the salt - complexed polymer, when the ion-coordinating atom in the B block material is oxygen, it is preferred that the oxygen for cation binding to cation concentration in the electrolyte should be between 4:1 and 50:1.

The polymeric electrolyte according to the invention is preferably
15 a solid, in the sense of resisting creep during cell assembly.

The electrolytes described herein may be used in any application where a solid solution electrolyte is possible and desired. One such application is in a galvanic or photogalvanic cell comprising an anode, a cathode and an electrolyte sandwiched between the said electrodes,
20 in which the electrolyte comprises a polymeric electrolyte according to the invention described herein. In a third aspect of this invention there is provided a battery comprising a plurality of such cells. The galvanic cells and batteries of such may be manufactured in known ways. They may be either primary or secondary (rechargeable) cells
25 or batteries for a variety of applications for example, electric vehicles, back-up power sources for use in for example computers, heart pacemakers and integrated power sources for electronic circuitry. The batteries may be connected in either series or parallel or a combination of such depending on whether maximum voltage or current or some compromise
30 is required as output.

The thickness of the individual cells can be made extremely small while maintaining a high contact surface area, and it is thus possible to incorporate many cells, for example 1000 or more, in a compact battery structure. For high energy density cells it is preferred that
35 the anode is lithium metal or an alloy for example, lithium-aluminium or lithium-silicon so that the anode is reversible to the Li/Li^+ couple.

Here it is preferred that the ABA triblock copolymer electrolyte is complexed with a lithium salt and that the cathode is a lithium ion intercalation material, such as TiS_2 , although an electrolyte and possibly conducting particles such as carbon black may be mixed with the cathode material. Thus the anode and cathode may be conventional as may the encapsulation of the cell and/or its assembly within the battery. For example, the cell may be formed using the techniques described in US Patent 4303748.

The polymers of the invention may also be used in a heterogeneous phase process, for example, solute separation and extraction, wherein a salt complexed with the B-phase should not be required. The solute to be concentrated in the stationary phase formed entirely or in part by a polymer of this invention may be for example an ionic salt or an organic material or an inorganic material or combination of such, possibly covalently bound together. The solute in solution could for example be passed through a column containing such a polymer. The polymer could be rendered less soluble in such an application by cross-linking in the A block.

An analogous use for the polymers of this invention is where the polymer would act as a membrane between different, usually liquid and solid phases forming a semi-permeable barrier allowing physical contact and transfer of material between said phases.

The invention will now be illustrated by way of example only with reference to the accompanying Figures 1-8 which show the temperature dependance of the conductivity of polymeric electrolytes of the invention.

The epoxide containing product (II) thus formed, was reduced with LiAlH_4 in THF solution. 0.08g LiAlH_4 was mixed with 40 cm^3 of purified THF followed by the addition of (II) (0.22g) in THF solution. After a 2.5 hour reflux, distilled water was added to react with excess hydride present and subsequently THF removed under vacuum. Water (40 cm^3), hydrochloric acid (2 mol^{-3} , 10 cm^3) to dissolve inorganic matter, and CH_2Cl_2 (80 cm^3) were added to the product mixture. After stirring for ca. 30 minutes to allow polymer dissolution the aqueous layer was discarded and the organic fraction washed with water several times. The polymeric product (III) was precipitated by pouring into methanol, dried and redissolved in CH_2Cl_2 . The solution formed was dried using molecular sieves and the polymer isolated by precipitation into methanol. The product (III) was dried under vacuum at 60°C .

III had 30% of all aliphatic B-block double bonds hydroxylated, as determined by ^1H nmr.

B Reaction of 52% of available C=C groups.

The method was similar to that above; 5g of the starting polymer (I) was reacted with 8g m-chloroperbenzoic acid in dichloromethane. NMR showed 52% epoxidation in the product isolated.

The reduction of the polymeric epoxide was similar to A above except that the isolated hydroxylated product was soluble in methanol preventing the use of a reprecipitation purification route. Instead the CH_2Cl_2 product solution obtained was evaporated down and residual water present poured off. The polymer was redissolved in CH_2Cl_2 , dried over molecular sieves, and the solvent removed. Product (III), 52% hydroxylated was finally dried under vacuum at 50°C .

C Functionalisation of Methoxy Polyethylene Glycol for grafting to the Hydroxylated ABA Triblock Copolymer (III)

Two routes of functionalisation were employed so that either an ether or urethane linkage could eventually be used to generate the required electrolyte forming polymer. The methods

allow easy variation of the eventual sidechain length by simple choice of the polyethylene glycol mass range to be used.

a. Formation of a tosylate

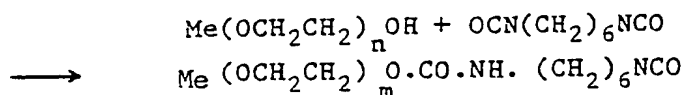
The method was that of Harris et al, J.Polym.SCI., Polym.Chem.Ed., 1984, 22,341.

3g of tosyl chloride in CH₂Cl₂ (20 cm³) was added dropwise to dried methoxy polyethylene glycol of average molar mass 350 (5g) and triethylamine (2g) in CH₂Cl₂ (25 cm³) at 0°C. After the solution had been stirred for 3 hours, a precipitate of triethylamine hydrochloride could be removed when the solution had been added to diethyl ether. Removal of solvent from the product solution and addition again to diethyl ether allowed separation of residual hydrochloride salt. The final product is labelled (IV).

In a similar manner methoxy polyethylene glycol of average molar mass 750 was tosylate functionalised, the product is labelled (XI).

b. Formation of a urethane

The reaction used was:



Methoxy polyethylene glycols of average molar mass ranges of 550 and 750 were used.

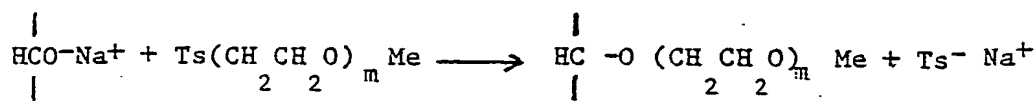
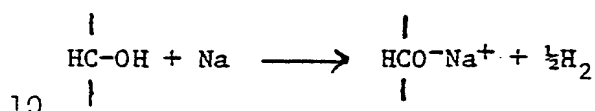
Hexamethylene diisocyanate (11 cm³, 5 molar excess) and two drops of dibutyl tin dilaurate were dissolved in a small quantity of THF stirred under nitrogen and methoxy polyethylene glycol (550, 7g) in THF solution added dropwise over a period of 5 hours. The reaction solution was stirred for ca. 15 hours, solvent removed and the liquid obtained added dropwise to dry diethyl ether maintained at -5 to -10°C. Decantation of the ether left the required product, (V). The precipitation procedure was repeated 3 times.

For the reaction of methoxy polyethylene glycol of average molar mass 750, a 9g sample was added to 11 cm³ of

hexamethylene diisocyanate in the presence of dibutyl tin dilaurate. The procedure used was that given above, and the product (VI) isolated in a similar way.

5 D Graft Copolymer formed between (III) with 30% Hydroxylation and (IV).

The reaction scheme used is summarised by the equations:



15



Excess sodium metal was added to a stirred THF solution
20 of (III) with 30% hydroxylation. The solution was decanted into a second vessel and excess (IV) in THF solution added. The reaction solution was stirred for 2 days at room temperature, after which the solvent and any remaining (IV) were removed. The polymeric product (VII) was washed with methanol and dried under
25 vacuum. Oxyethylene grafting was confirmed by n.m.r.

E Graft Copolymer (XII) formed between (III) with 52% hydroxylation and (XI).

30 In an analogous manner to the synthesis described in D above, (III) with 52% hydroxylation, in stirred THF solution, was reacted with sodium metal to generate the salt, which after separation was allowed to react with the tosylate (XI). The product isolated is labelled (XII).

35

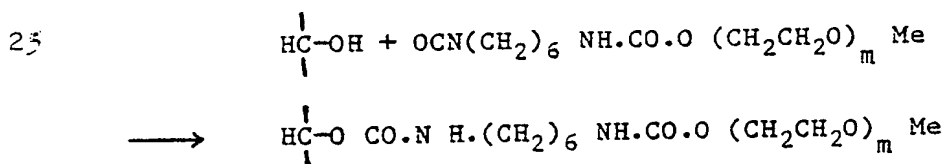
Example 2Graft Copolymers formed from the Reaction of (III) with (V) or (VI)

The method involves a condensation reaction to generate a urethane linkage at the grafting site. A dibutyl tin dilaurate catalyst was used.

A 2.5g of (V) in THF solution was added to (III) 30% hydroxylated (0.2g) in THF followed by 2 drops of dibutyl tin dilaurate catalyst. The resulting solution was refluxed for ca. 16 hours, after which the solvent was evaporated off and the solid remaining washed with methanol several times in order to remove residual (V). The polymeric product, (VIII) was dried under vacuum at 50°C and contained a ca. 52% wt grafted oxyethylene component.

B 3g of (VI) in THF solution was added to (III) 30% hydroxylated (0.25g) in the presence of dibutyl tin dilaurate in THF solution. Following a ca. 16 hour reflux the solvent was removed and the crude product remaining washed with cold methanol then redissolved in CH₂Cl₂. The product was reprecipitated by pouring into cold methanol and dried under vacuum at 60°C. The final product, (IX) had a 64% wt oxyethylene component, confirmed by nmr.

The reactions may be summarised by the equation:



C A graft copolymer formed between (III) with 52% hydroxylation and (V).

3g of (V) was dissolved in THF and added to a solution of 0.25g (III) (52% hydroxylated) and 2 drops of dibutyl tin dilaurate in THF. The resulting solution was refluxed for 16 hours. After evaporation of the solvent the remainder was washed repeatedly with cold (0°C) methanol to remove excess

(V). Incorporation of the polyglycol in the product formed, (X) was confirmed by nmr, showing a 63% wt oxyethylene component.

D In an analogous manner a graft of (III) 52% hydroxylated with (VI) was prepared. The product is labelled (XIII).

Example 3

Electrolytes from polymer (IX)

10 A film of (IX) having B-phase complexed with LiCF_3SO_3 (to give B-phase oxygen-for-lithium-binding to lithium molar ratio of either 50, 30, 16 or 7) was prepared from a THF solution of (IX) and the salt at room temperature. The solvent was evaporated under vacuum to leave a
15 solid electrolyte. This was heated to 110-120°C in vacuum for 4-5 hours. After cooling the sample to room temperature further manipulations were carried out under argon-atmosphere glovebox conditions. The material was mounted between electrode anvils and pressed at room temperature from a 5mm
20 diameter pellet to a 13mm diameter film. Finally, the films were heated to 110-120°C for 1 hour, without the application of pressure, then slowly cooled (ca. 1°C min⁻¹) to room temperature. The electrodes - electrolyte film assembly was transferred to a variable-temperature conductivity cell for ac
25 impedance analysis. The electrodes were steel and ion-blocking. Films examined were typically 100-300 μm in thickness and their response characteristics were recorded over a frequency range of 1 MHz to 1 Hz, at a series of
30 temperatures. Log₁₀ (conductivity/S cm⁻¹) against reciprocal temperature (K⁻¹) is plotted in Fig 1.

The film with an O/Li ratio of 16 had a conductivity at 25°C of 1×10^{-5} S cm⁻¹,

while that with O/Li = 7 exhibited a value of $5.8 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C, and had a B-phase glass transition temperature of -37°C, recorded with a 20°C min⁻¹ heating rate.

Example 4

5 Electrolytes from polymer (VIII)

The polymer was milled at close to -196°C and then milled under similar conditions with an appropriate quantity of LiCF₃SO₃ added so that a homogeneous material was generated. This is an alternative first step to the solvent casting
10 procedure used in Example 3. Subsequent steps of heating, pressing at room temperature, and heating followed by a slow cool to room temperature were as described in Example 3, as was the electrolyte film ac impedance examination. Films having
15 O/Li ratios of 30, 16 and 7 were investigated and the dependence of their conductivities is described in Fig 2. With O/Li = 16 the electrolyte had a conductivity at room temperature of $2.7 \times 10^{-6} \text{ S cm}^{-1}$.

An electrolyte was prepared by a solvent casting route similar to that of Example 3, except that the solvent used for (VIII)
20 and LiCF₃SO₃ (to give O/Li = 7) was nitromethane with ca. 5%v/v THF. The solution was allowed to evaporate under a flow of dried nitrogen to leave a film coating one of a pair of steel electrodes. Residual solvent was removed at 130°C for 24 hours. The temperature
25 dependence of conductivity for the electrolyte is recorded in Fig 3 and the values are approximately one order of magnitude greater than those of the equivalent electrolyte prepared by the milling procedure described above, demonstrating the importance of electrolyte or polymer forming route on the properties of the final
30 material. At 25°C (VIII) with O/Li = 7 (LiCF₃SO₃) showed a conductivity of $2.0 \times 10^{-5} \text{ S cm}^{-1}$.

Example 5

Electrolytes from (X)

An electrolyte was prepared in a similar manner to
35 those described in Example 4, by solid-state milling and press-

ing. A plot of \log_{10} (conductivity/S cm^{-1}) versus reciprocal temperature (K^{-1}) for an electrolyte with O/Li = 16 is given in Fig 4. At 25°C the conductivity was 4.0×10^{-6} S cm^{-1} .

5 Example 6

Electrolytes from (XII)

Electrolyte films were prepared in a similar way to those of Example 3. A film of (XII) containing LiCF_3SO_3 to a concentration resulting in a B-phase O/Li molar ratio of 16 had
10 a conductivity at 25°C of 1.0×10^{-5} S cm^{-1} .

Example 7

Blending of ABA triblock polymer: (a) with A - block compatible material.

0.028g of polystyrene ($M_n = 20,2000$, $M_w = 20,800$) was dissolved
15 with 0.1g of (IX) and LiCF_3SO_3 (to give O/Li = 7) in a small volume of dichloromethane and the solvent removed by evaporation. For the generation of electrolyte films the material was treated in a similar manner to (IX) in Example 3 and the conductivity was measured as a function of temperature (Fig 5). The material had an oxyethylene
20 component of 50% wt. At 25°C a conductivity of 6.7×10^{-6} S cm^{-1} was recorded.

0.052g of polystyrene ($M_n = 20,2000$, $M_w = 20,800$) was dissolved in dichloromethane with 0.1g of (IX) and sufficient LiCF_3SO_3 to give O/Li = 7. The film formed by evaporation was treated in a similar
25 way to the example above with a 50% wt oxyethylene component. At 25°C a conductivity of 1.4×10^{-6} S cm^{-1} was recorded (Fig 5) and the material had an oxyethylene content of 42% wt.

(b) With B - block compatible material.

0.1g of (IX), 0.05g of polyethylene glycol dimethyl ether of average molar mass 350 and sufficient $\text{Li CF}_3\text{SO}_3$ (to give $\text{O/Li} = 7$) in THF solution was evaporated at room temperature to form a solid electrolyte film. This was then heated under vacuum for 4 hours at 120°C , cooled to room temperature, pressed between cell electrodes as described in example 3, and the conductivity recorded. At 25°C the electrolyte had a conductivity of $4.1 \times 10^{-5} \text{ S cm}^{-1}$.

10 Example 8

Use of polymer in a heterogeneous phase process..

0.30g of (VIII) was immersed in a solution of 0.070g $\text{Li CF}_3\text{SO}_3$ in methyl alcohol (3 cm^3) for ca 30 minutes to allow partition of the salt between the B - block and the methyl alcohol phase.

15 The (VIII) was removed from the methanol and dried under vacuum. Atomic absorption spectroscopy showed the ca 80% of the total salt content initially in the methanol phase had partitioned into the polymer.

20 The morphology of the above polymers, of domains of the polystyrene A phase dispersed in a matrix of the polybutadiene-derived B phase was confirmed by electron microscopy.

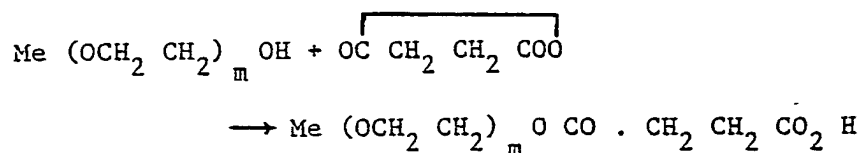
Example 9

Graft copolymer formed between III with 30% hydroxylation and methoxypolyethylene glycol carboxylic acid functionalised

- 5 A Functionalisation of Methoxypolyethylene glycol by reaction with succinic anhydride.

The general procedure is described by Zalipsky et al (European Polymer Journal, 1983, 19, 1177).

- 10 Overall:



XIV

- 15

Method 1

- 7 g of dry methoxy polyethylene glycol (750) and a 4 fold molar excess of succinic anhydride (3.72 g) were dissolved in a small amount of toluene and stirred at 150°C for 5 hours. On cooling, the functionalised product, (XIV) with glycol mass 750, could be precipitated out of solution by addition to cooled diethyl ether. This purification step was repeated several times.
- 20

Method 2

- 25 A catalysed procedure.

- To 7 g of dry methoxypolyethylene glycol (750) in THF was added 1 g of succinic anhydride, 1.3 cm³ triethylamine and 1.14 g 4-dimethylamino-pyridine (DMAP) and the solution stirred overnight at room temperature. The solvent was removed under reduced pressure, carbon tetrachloride added, the solution formed filtered and subsequently the product was precipitated by pouring the solution into cooled diethyl ether. The nature of the product and its association with DMAP was confirmed by ir spectroscopy (Zalipsky et al).
- 30

- 35 B Graft copolymer (XV) formed between (III) with 30% hydroxylation and (XIV) with glycol mass 550.

0.1 g of (III) with 30% hydroxylation and 0.4 g of (XIV) with glycol mass 550 were dissolved in dichloromethane. To this was added 0.1 g

dicyclohexylcarbodiimide (DCC) and a catalytic quantity of 4-pyrrolidinopyridine. The solution was refluxed for 2 hours. After cooling, precipitated dicyclohexylurea (DCU) was filtered off and the residue dried and dissolved in acetone. Further DCU residues were separated from the solution. The graft copolymer product was purified further by precipitation from THF solution into cooled methanol. The product, (XV), was characterised by ir and nmr spectroscopies.

Example 10

1.0 Electrolytes from (XV), and analogue (XVI) with glycol mass 750, both prepared by the route given in Example 9

(XVI), with 30% grafting of methoxypolyethylene glycol 750 through a succinate linkage prepared by the method of Example 9, was dissolved in a 90% v/v nitromethane-THF mixture and $\text{Li CF}_3 \text{ SO}_3$ added to give a B-phase oxygen-to-lithium ion molar ratio of 7. A film was cast from the solution onto the lower of a pair of horizontal parallel steel electrodes. After the majority of the solvent had evaporated the film was heated for 10 hours at 100°C . A further heating period was occasionally applied. Conductivity was recorded for film ca 250 μm in thickness. $\log_{10}(\text{conductivity}/\text{S cm}^{-1})$ versus reciprocal temperature (K^{-1}) is plotted in Figure 6. A similar result was obtained for an electrolyte prepared by a similar route from (XV) with an oxygen-to-lithium ion molar ratio of 7. Data is given in Figure 7.

Example 11

2.5 Blend formed between high molar mass polyethylene oxide and (VIII) in the presence of $\text{Li CF}_3 \text{ SO}_3$ to form an electrolyte

Polyethylene oxide (mass 4×10^6), graft copolymer (VIII) and $\text{Li CF}_3 \text{ SO}_3$ (to give an oxygen-to-lithium ion molar ratio of 10) were ground together in a ball-mill at liquid nitrogen temperatures. Mixtures were prepared containing 25 or 50% wt polyethylene oxide, based on total polymer content. The blend so formed was hot pressed to give an electrolyte film by heating the material between steel electrode plates at 373 K using slight pressure. The temperature dependence of conductivity for the two samples is given in Figure 8.

Example 12.Synthesis of a polystyrene-polyethylene oxide-polystyrene ABA triblock copolymer.

A The synthesis was achieved by first anionically polymerising
5 styrene by a living polymeric route using techniques developed by
Szwarc (J H Richard and M Szwarc, Trans. Farad. Soc., 1959, 55, 1644)

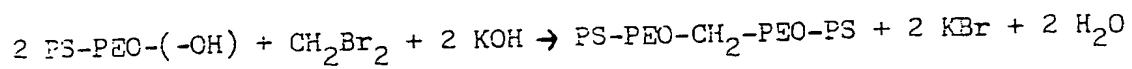
Firstly the vacuum line polymerisation system was washed and
cleaned with distilled toluene, styrene and secondary butyl lithium
initiator, giving a living polymerisation solution. This solution
10 was returned to a separate flask. The process was repeated using
measured quantities of sec. butyl lithium (8.4×10^{-4} mol) and styrene
(8.71g, 0.084 mol). After 24 hr, excess ethylene oxide (3.25g, 0.074
mol) was added to the 'living polymer' solution. The formerly red,
now colourless solution was left overnight before final termination
15 with methanol. The resultant polystyrene ethylene oxide end-capped
polymer was isolated by pouring the reaction solution into a 16 -
fold excess of n-heptane. The product was a colourless granular sol-
-id, and gpc at 70°C with DMA eluant showed $M_w = \text{ca. } 15,000$ and
 $M_w / M_n = 1.14$.

20 B Formation of a polystyrene-polyethylene oxide diblock copolymer.

Dry THF (30 ml) was distilled from sodium benzophenone into a
thick-walled ampoule containing the polystyrene polymer prepared in
step A above (1.02g, 5.1×10^{-5} mol). A solution of potassium metho-
xide (5.1×10^{-5} mol) in dry THF (14.3 ml) was transferred under
25 nitrogen to the ampoule and the solvent removed by vacuum transfer
overnight. Ethylene oxide (6.8g, 0.154 mol) was distilled into the
ampoule, which after degassing, was sealed under vacuum and heated
at 70°C for 9 days. The resultant product was a colourless wax-like
solid, obtained after cooling and isolation with $M_w = 110,000$ and
30 containing 14 % polystyrene. The molar mass of the product and the
individual block lengths of the product polymer could be varied
using known methods.

C Formation of the polystyrene - polyethylene oxide - poly-
styrene ABA triblock copolymer by coupling the -OH termini of the
35 ethylene oxide blocks of the diblock polymer prepared in B above.

The preparative route of step C is summarised by the equation:



5 The procedure was a modified Williamson ether synthesis, as described in GB 8520902-A, and involves the generation of a methylene group as the linkage. Gel permeation chromatography confirmed the approximate doubling of the molar mass to Mw ca. 200,000 relative to the starting polymer of step B.

10

15

Key (where necessary) to Figures 1 - 8

- Fig 1. O:Li = 7:1 = ▲
 O:Li = 16:1 = X
 5 O:Li = 30:1 = ●
 O:Li = 50:1 = ■
- Fig 2. O:Li = 7:1 = ▲
 O:Li = 16:1 = ●
 O:Li = 30:1 = X
- 10 Fig 3. Pressed, O:Li = 7:1 = X
 Cast from nitromethane, O:Li = 7:1 = ▲
- Fig 5. Wt. % of ABA triblock polymer } 64 = X
 in polymer/polystyrene mixture. } 50 = ●
 } 42 = ▲
- 15 Fig 8. 25 wt% polyethylene oxide = ■
 50 wt% = +

Claims

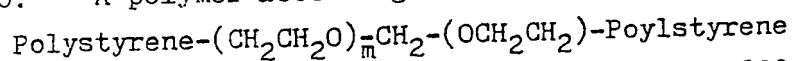
1. A polymer, being an ABA triblock polymer, the A block material being rigid having a transition away from its rigid phase above 70°C, the B block material being wholly or partly ion-coordinating, elastomeric or amorphous, the B/A block length ratio being greater than 1, and in which phase separation between the A and B blocks may or may not occur.
2. A polymer according to claim 1, characterised in that the B block material contains polyoxyethylene $(\text{CH}_2\text{CH}_2\text{O})_m$ sequences, where m is an integer, epoxide groups or hydroxy groups.
3. A polymer according to claim 2 characterised in that the B block contains polyoxyethylene sequences, said sequences being in a side chain or cross link attached to the B block main chain, and m is 2 to 22.
4. A polymer according to claim 2 characterised in that the B block material contains polyoxyethylene sequences, said sequences being in the B block main chain, $(\text{CH}_2\text{CH}_2\text{O})_m$ where m is an integer 3 to 3000.
5. A polymer according to claim 3 characterised in that the B block material has a structure which is a cis-1,4 polybutadiene chain in which a proportion of CH=CH unsaturated sites are replaced by:

$$-\text{CH}_2-\overset{|}{\text{CH}}-\text{X}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{R}$$
sites where X is a linking group and R is hydrogen or $\text{C}_1 - 6$ alkyl, and the A block material is selected from polystyrene, poly(α -methylstyrene), polyurethanes and poly(p-xylylene).
6. A polymer according to claim 5 characterised in that the polyoxyethylene sequences are linked to the B block main chain via links X which are or include ether links $(-\text{O}-)$, methylene links $(-\text{CH}_2-)$, ester links $(-\text{COO}-)$, urethane $(-\text{NHCOO}-)$ or combinations of these.
7. A polymer according to claim 6 characterised in that the links X are selected from $-\text{O}-$, $\text{OCONH}(\text{CH}_2)_n\text{NHCOO}$ where n is 2 to 12, and $-\text{OCO}-(\text{CH}_2)_p\text{COO}$ where p is 1 to 12, and R is methyl.
8. A polymer according to claim 6 characterised in that the A block material is polystyrene.
9. A polymer according to claim 7 characterised in that the A block material is polystyrene.

10. A polymer according to claim 9 characterised in that the average molar mass of the A block segments are 10,000 to 40,000 each and of the B block segment about 40,000 to 150,000.
11. A polymer according to any one of claims 1, 2, 3 or 4 characterised in that the polymer is additionally blended with one or more materials that are compatible with the A block material or/and with the B block material.
12. A polymer according to claim 5, characterised in that the polymer is additionally blended with polyethylene glycol dimethyl ether or polystyrene or high molar mass polyethylene oxide.
13. A polymer according to claim 1 characterised in that it has a structure based upon an ABA triblock polymer in which the A block is selected from polystyrene, poly(α -methylstyrene), polyurethanes and poly(p-xylylene) and the B block is a poly cis 1, 4 -butadiene chain in which a proportion at least of the HC=CH sites in the B block are replaced by $\text{CH}-\text{CH}$ or $\text{HC}-\text{CH}_2$ sites.

$$\begin{array}{ccc} & \text{O} & \text{OH} \\ & | & | \\ \text{CH}-\text{CH} & & \text{HC}-\text{CH}_2 \end{array}$$
14. A polymer according to claim 13 characterised in that the A block is polystyrene.
15. A polymer according to claim 4 characterised in that the polymer has a structure wherein the A block is selected from polystyrene, poly(α -methylstyrene), polyurethanes and poly(p-xylylene) and the B block consists wholly or partly of polyoxyethylene ($\text{CH}_2-\text{CH}_2\text{O}$)_m sequences or of polyoxyethylene sequences joined by linker groups.
16. A polymer according to claim 15 characterised in that the A block is polystyrene.
17. A polymer according to claim 16 characterised in that the average molar mass of the A block segments are about 10,000 to 40,000 each and of the B block about 40,000 to 150,000.
18. A polymer according to claim 16 characterised in that the B block consists of two ($\text{CH}_2\text{CH}_2\text{O}$)_m segments joined by a linker group.
19. A polymer according to claim 18 characterised in that the linker group is or includes ether, methylene, ester, urethane, (CH_2)_n NHCOO or oxymethylene OCH₂ groups.

20. A polymer according to claim 19 having a structure:



where the sum of the m's is in the range 3 to 3000, each m being an integer.

21. A polymeric electrolyte characterised in that it consists of a polymer as claimed in any one of claims 1 to 10 or 12 to 20 having additionally one or more ionic salts complexed with the B block.

22. A polymeric electrolyte according to claim 21 characterised in that the ionic salt is LiCF_3SO_3 .

23. A polymeric electrolyte according to claim 21 characterised in that the electrolyte is additionally blended with one or more materials that are compatible with the A or/and B block materials.

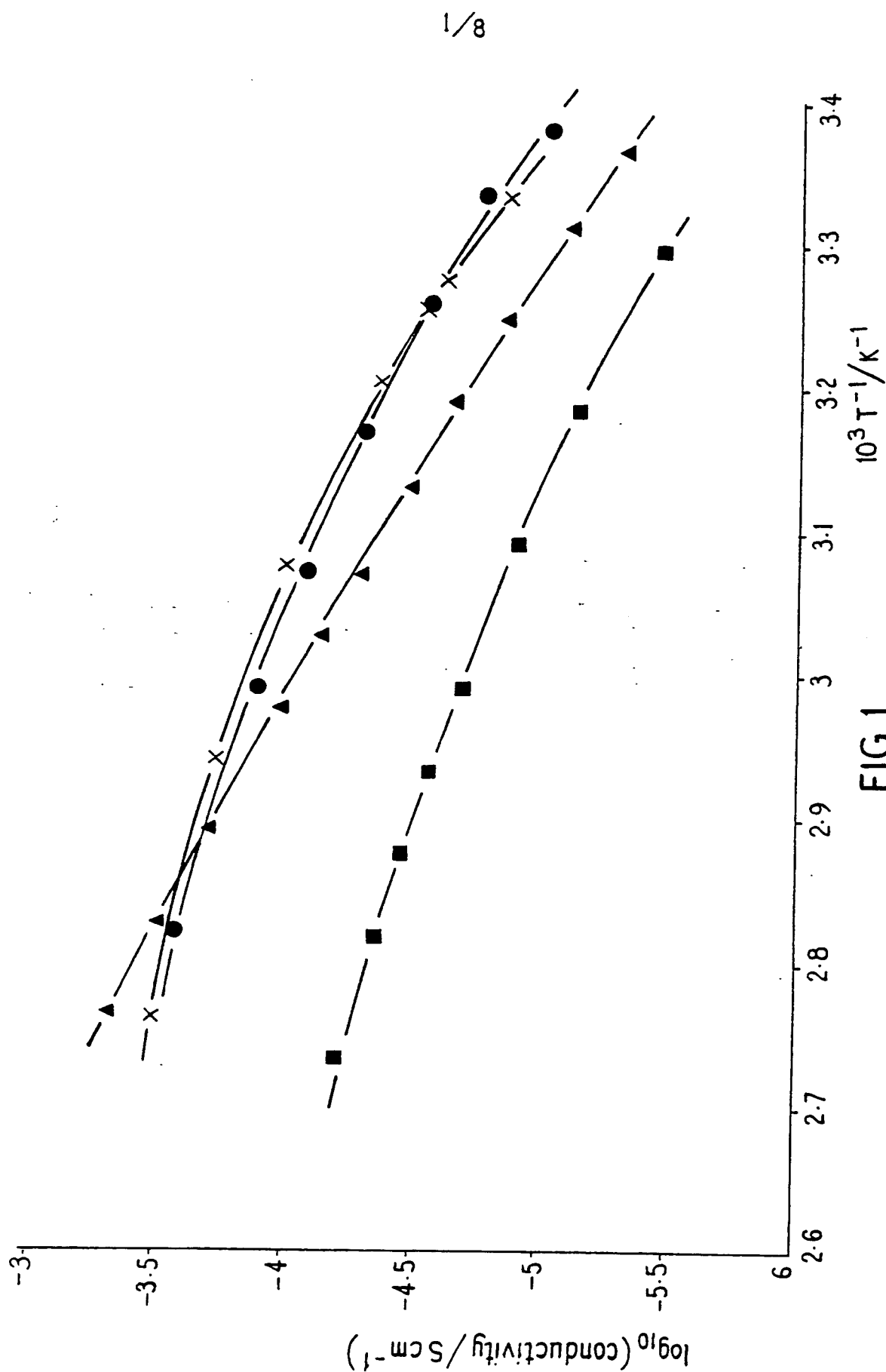
24. A polymeric electrolyte characterised in that it consists of a polymer as claimed in claim 11 having additionally one or more ionic salts complexed with the B block.

25. A method for separation of a solute from a solution, characterised in that it includes the steps of exposing the solution to a polymer as claimed in any one of claims 1 to 10 or 12 to 20 so that the solute is partitioned between the polymer and the solvent,

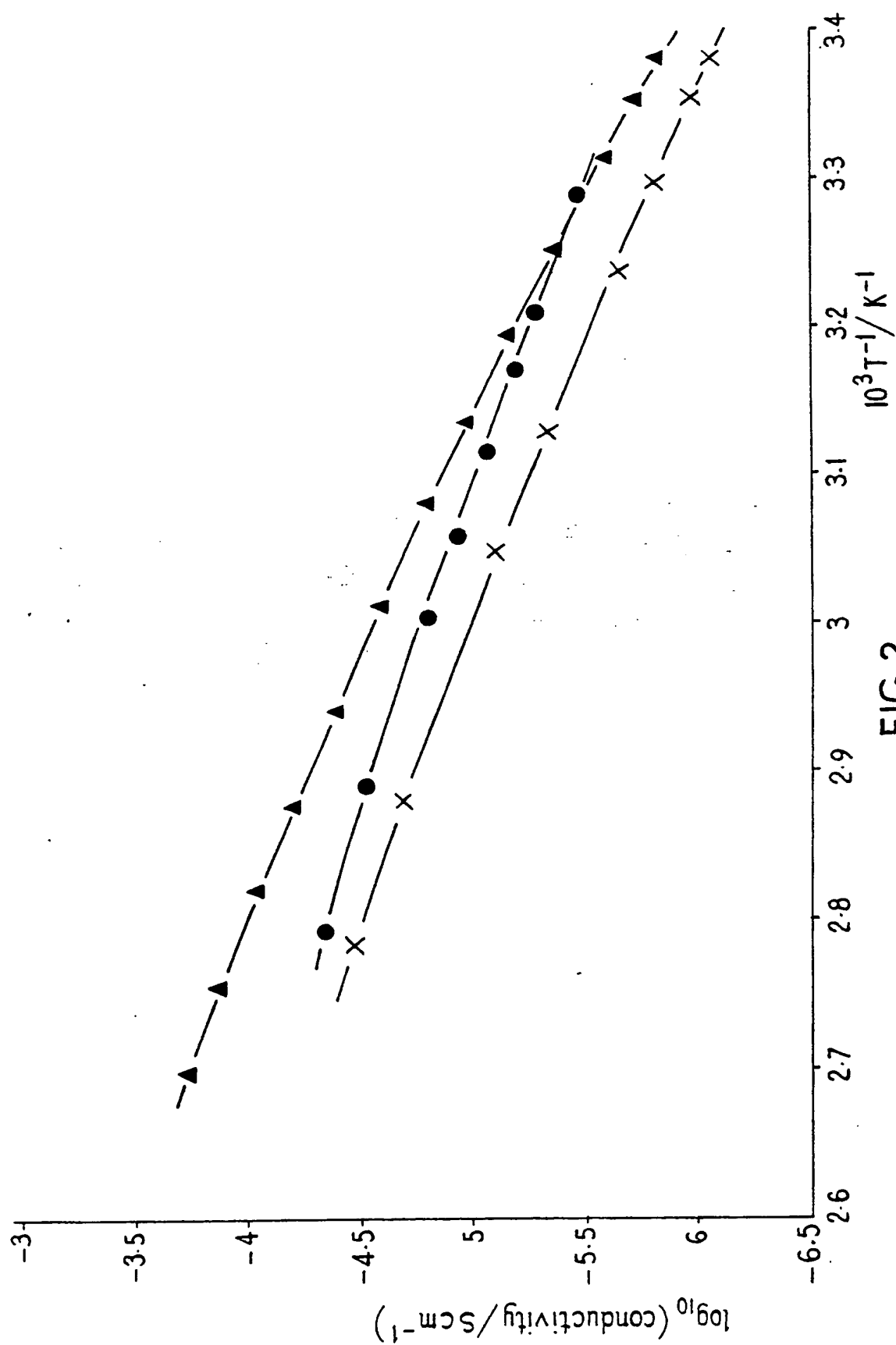
26. A method for separation of a solute from a solution, characterised in that it includes the steps of exposing the solution to a polymer as claimed in claim 11 so that the solute is partitioned between the polymer and the solution.

27. A method for the preparation of a polymer as claimed in claim 1, characterised in that it includes the step of grafting polyoxyethylene sequences of structure $-(\text{CH}_2\text{CH}_2\text{O})_{\overline{m}}\text{R}$ where R is hydrogen or alkyl containing 1 - 6 carbon atoms as side chains onto the B block of an ABA triblock polymer.

28. A method as claimed in claim 27 characterised in that the said ABA triblock polymer is a polystyrene-polybutadiene-polystyrene polymer.



2/8



3/8

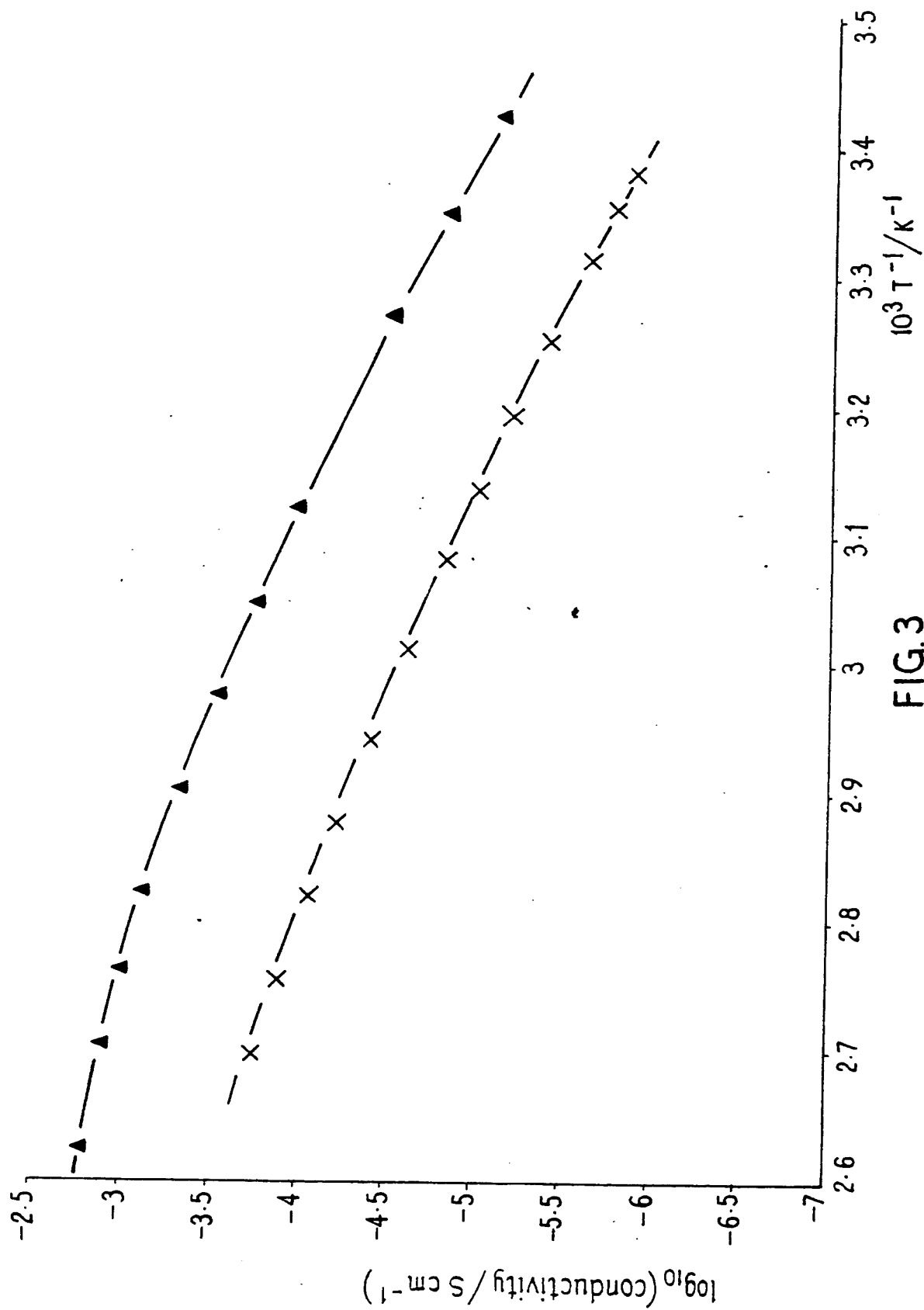


FIG.3

4/8

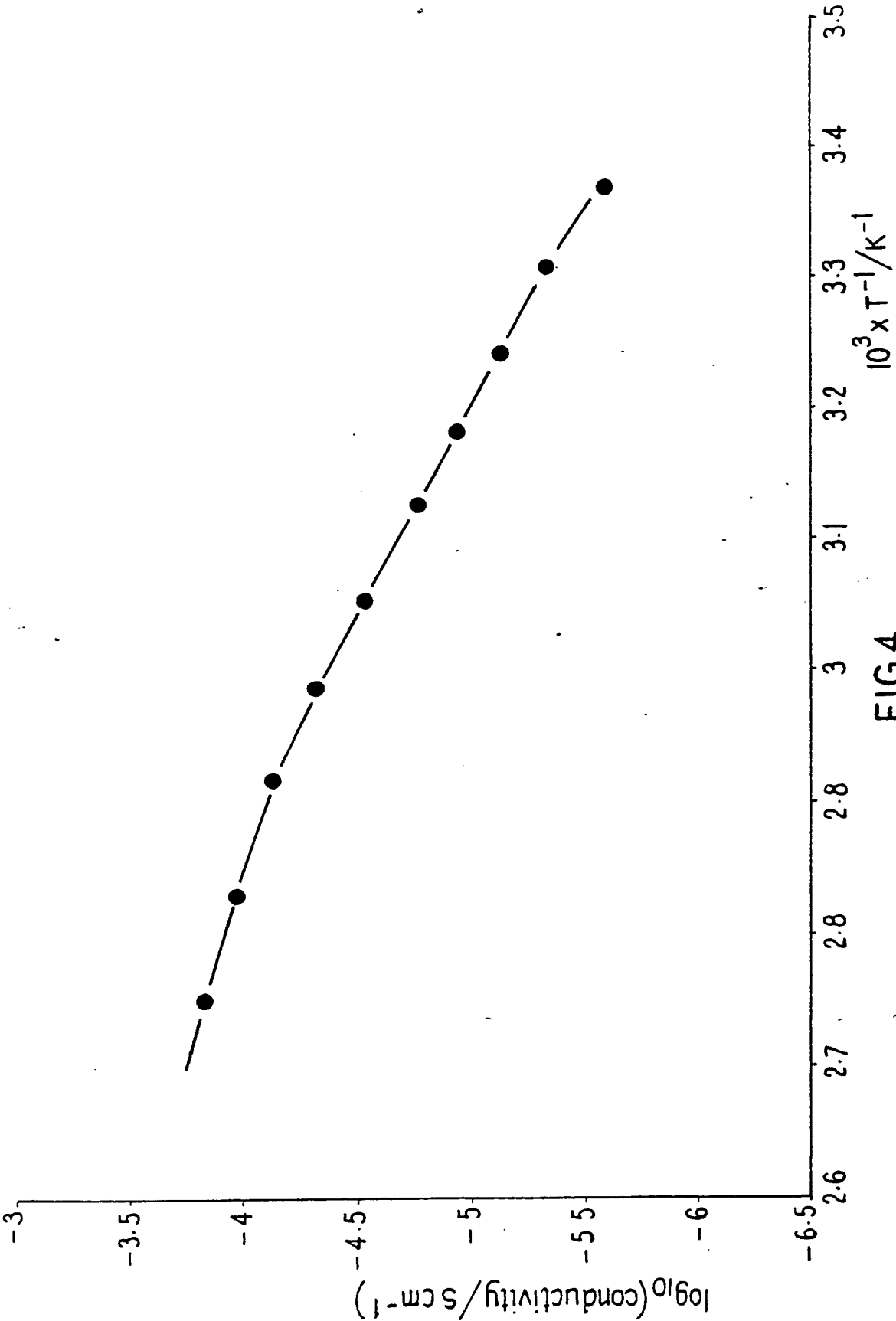
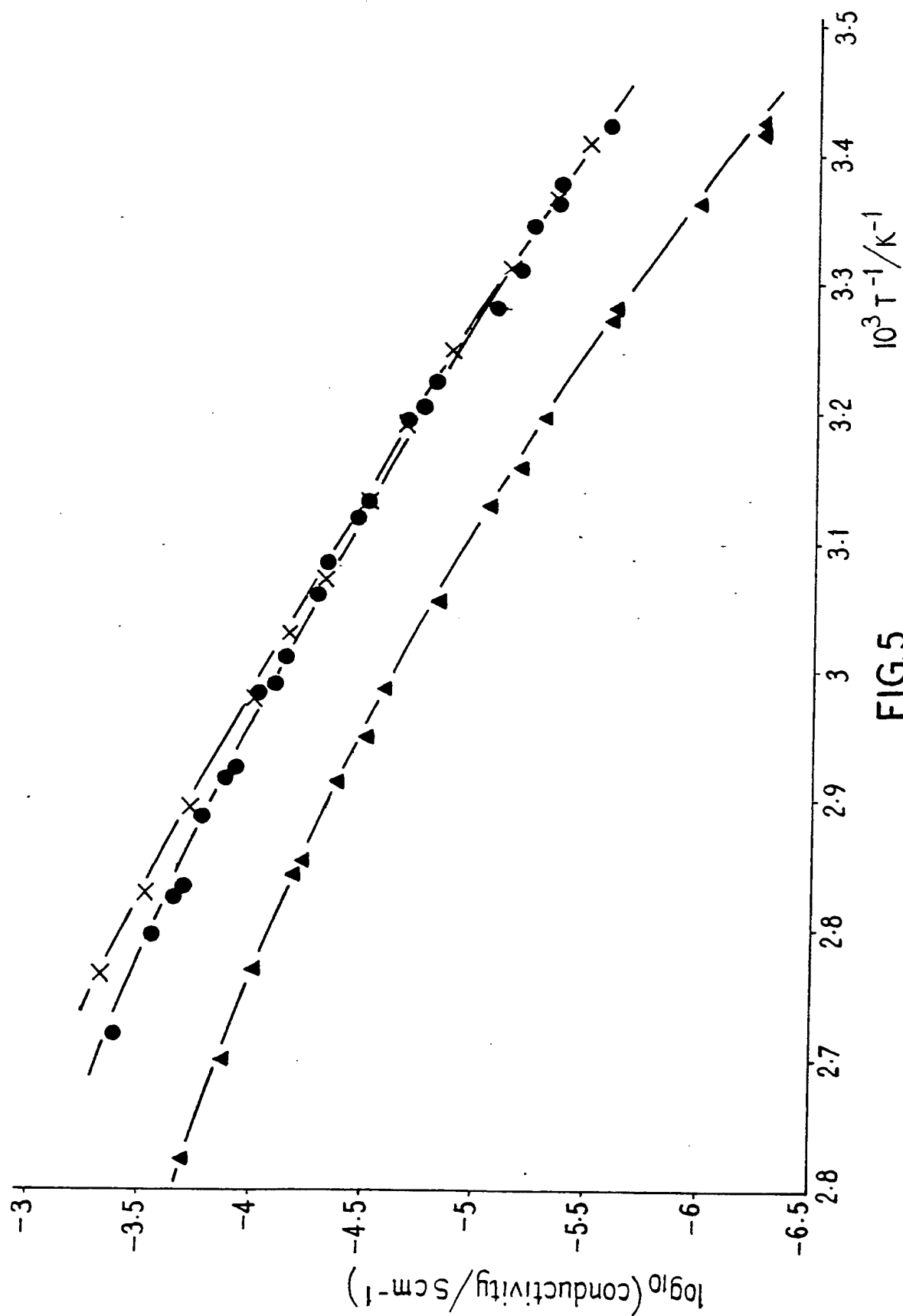


FIG.4

5/8



6/8

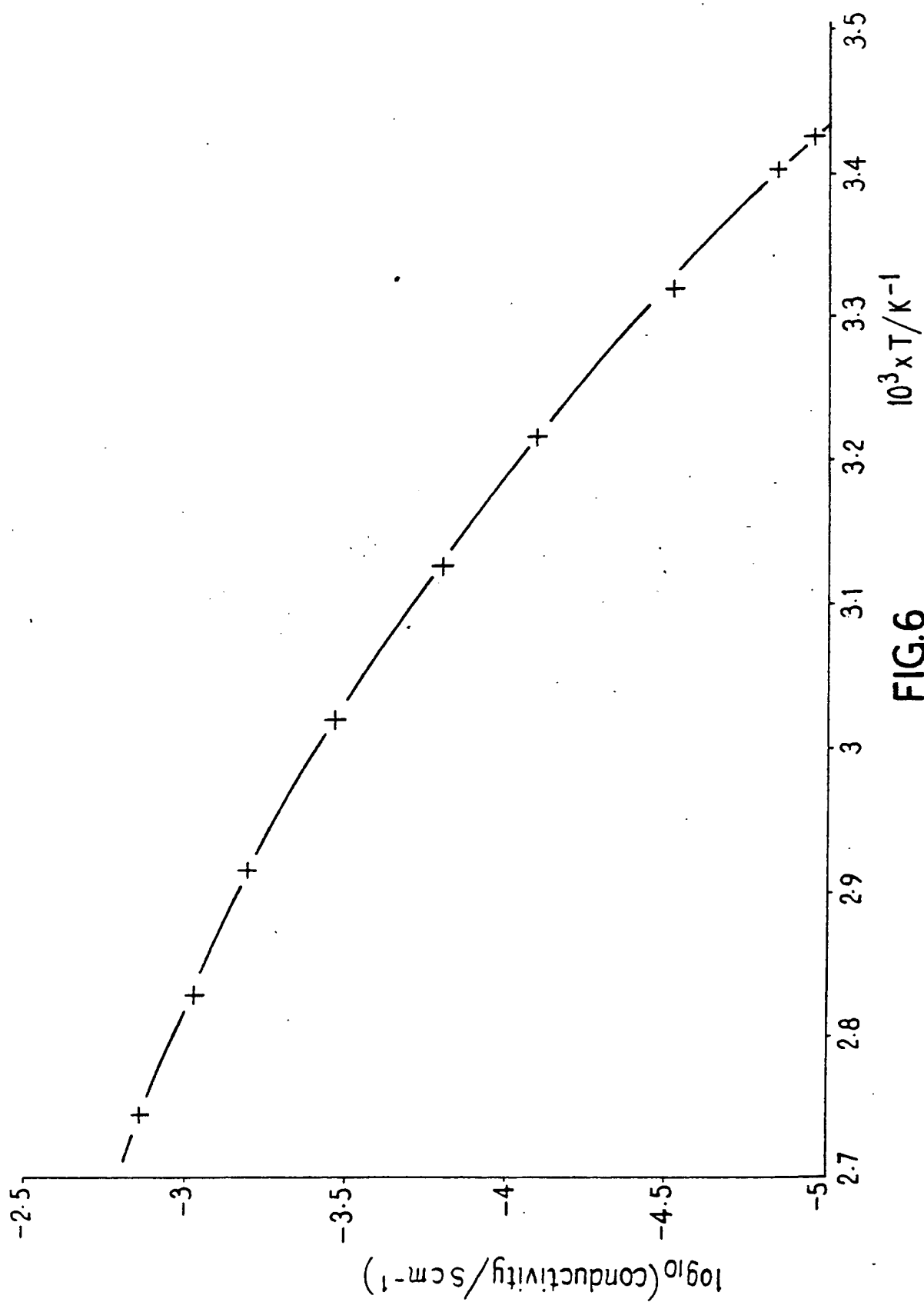


FIG.6

7/8

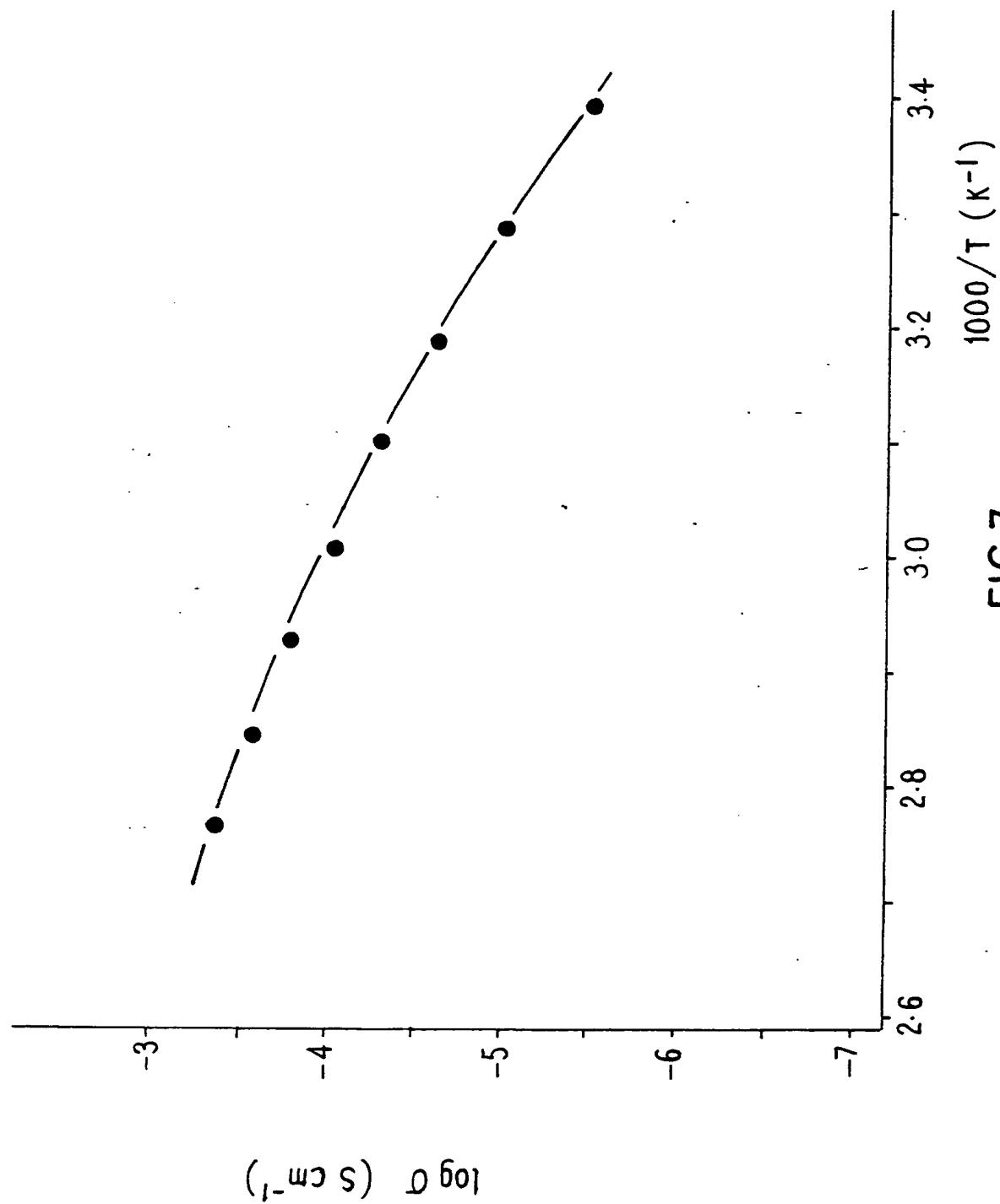
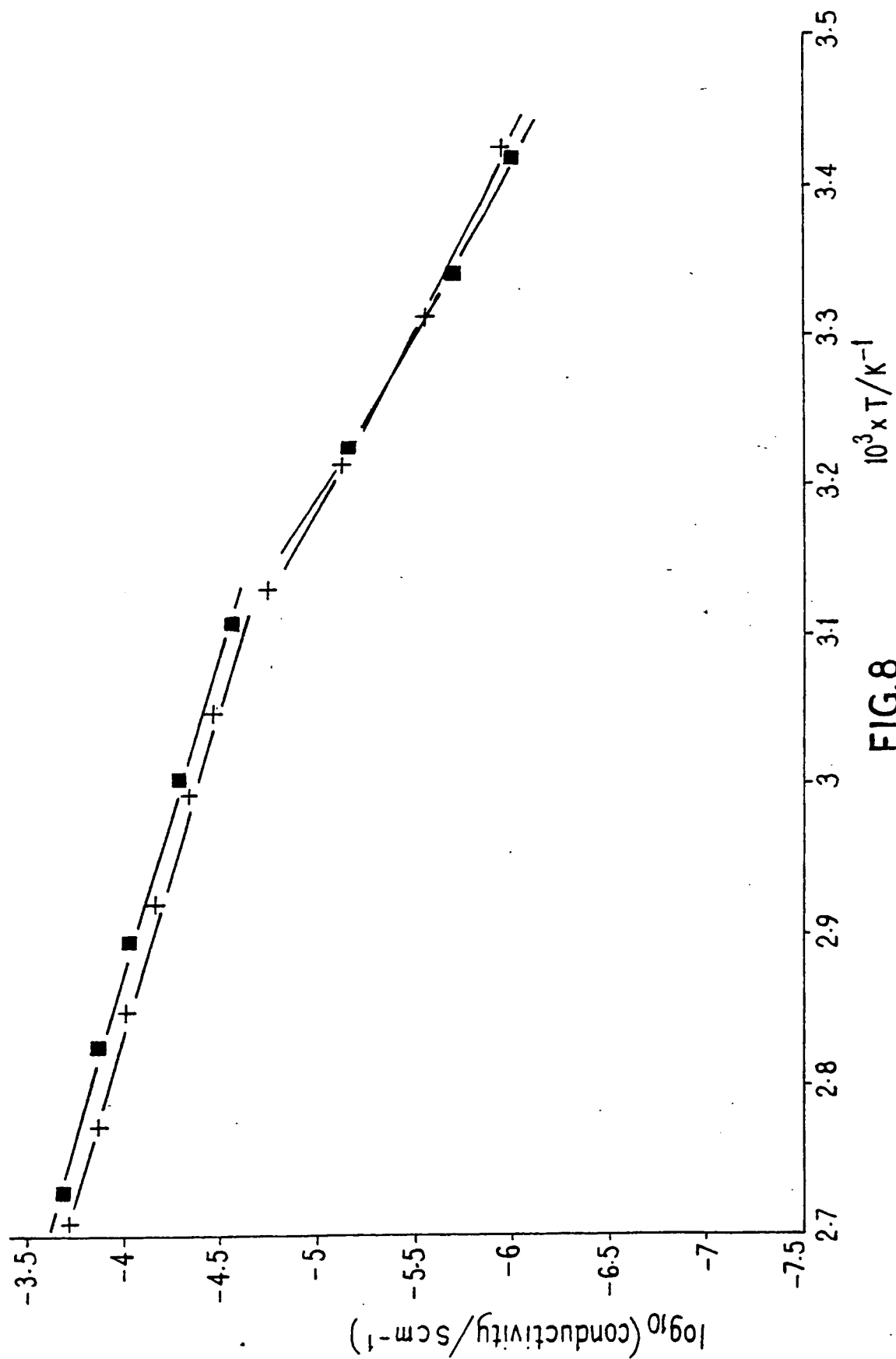


FIG.7

8/8



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 87/00759

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 08 G 81/02; H 01 M 6/18; C 08 G 65/08																	
II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding-bottom: 5px;">Classification System</td> <td style="border-bottom: 1px solid black; padding-bottom: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴</td> <td style="padding: 5px;">H 01 M; C 08 G</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	H 01 M; C 08 G											
Classification System	Classification Symbols																
IPC ⁴	H 01 M; C 08 G																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border: none;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; padding-bottom: 5px;">Category ¹⁰</th> <th style="width: 70%; border-bottom: 1px solid black; padding-bottom: 5px;">Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border-bottom: 1px solid black; padding-bottom: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">Bulletin de la Société Chimique de France, 1962, Masson & Cie., (Paris, FR), G. Finaz et al.: "Préparation de copolymères séquencés styrolène-oxyde d'éthylène", pages 262-266 see pages 262-264.</td> <td style="vertical-align: top; padding: 5px;">1, 2, 4, 15, 16</td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 3663659 (W.C. KRAY et al.) 16 May 1972 see claim 1</td> <td></td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 2164047 (THE SECRETARY OF STATE FOR DEFENCE (UNITED KINGDOM) 12 March 1986 see claim 1</td> <td></td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 10px;">-----</td> </tr> </table>			Category ¹⁰	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	Bulletin de la Société Chimique de France, 1962, Masson & Cie., (Paris, FR), G. Finaz et al.: "Préparation de copolymères séquencés styrolène-oxyde d'éthylène", pages 262-266 see pages 262-264.	1, 2, 4, 15, 16	A	US, A, 3663659 (W.C. KRAY et al.) 16 May 1972 see claim 1		A	GB, A, 2164047 (THE SECRETARY OF STATE FOR DEFENCE (UNITED KINGDOM) 12 March 1986 see claim 1		-----		
Category ¹⁰	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³															
X	Bulletin de la Société Chimique de France, 1962, Masson & Cie., (Paris, FR), G. Finaz et al.: "Préparation de copolymères séquencés styrolène-oxyde d'éthylène", pages 262-266 see pages 262-264.	1, 2, 4, 15, 16															
A	US, A, 3663659 (W.C. KRAY et al.) 16 May 1972 see claim 1																
A	GB, A, 2164047 (THE SECRETARY OF STATE FOR DEFENCE (UNITED KINGDOM) 12 March 1986 see claim 1																

<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding-bottom: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding-bottom: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 5px;">2nd February 1988</td> <td style="padding: 5px; text-align: center;">14 MAR 1988</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding-bottom: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding-bottom: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 5px; text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="padding: 5px; text-align: center;"> P.C.G. VAN DER PUTTEN </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	2nd February 1988	14 MAR 1988	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN							
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report																
2nd February 1988	14 MAR 1988																
International Searching Authority	Signature of Authorized Officer																
EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN																

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 8700759

SA 19236

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/02/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3663659	16-05-72	None	
GB-A- 2164047	12-03-86	WO-A- 8601643	13-03-86
		EP-A- 0190306	13-08-86
		JP-T- 62500334	05-02-87

EPB 10/10/88

THIS PAGE BLANK (USPTO)